DOE/PC/89771--4

DE91 002496

FOURTH QUARTER REPORT
July 1 - September 30, 1990

MECHANISM OF HYDRODENITROGENATION (Part 4)

INFRARED SPECTROSCOPY OF ACIDIC MOLYBDENA CATALYSTS

Raul Miranda
Department of Chemical Engineering
University of Louisville
Louisville, KY 40292, USA

contents

ABSTRACT

Mo oxide catalysts supported over a complete series of silica-aluminas have been characterized in the oxidic and reduced states, by means of total acidity measurements and by infrared spectroscopy. Ammonia chemisorption was used to titrate the total acidity of the catalysts, and IR absorption of adsorbed pyridine to distinguish Bronsted from Lewis acid sites. The formation of new acidity upon deposition of molybdena on silica-alumina supports was then explained on the basis of a simple surface model.

The new acidity is of both Lewis and Bronsted type, the preponderance of one over the other depending on support composition, as well as loading and state of oxidation of Mo. High-alumina supports and low Mo loading favor dispersed Mo species, in particular bidentate and monodentate di-oxo Mo species. The latter is responsible for the new Bronsted acidity. Coordinative unsaturation of polymolybdates is responsible for the new Lewis acidity, which is increased upon reduction of Mo. High-silica supports favor monodentate species (high Bronsted acidity) up to 4 wt% MoO_3. Beyond that, polymolybdate species and Lewis acidity predominate.

INTRODUCTION

Efficient nitrogen removal from heterocyclic aromatics in liquid fuels calls for the development of catalysts with better HDN activity than is available with the traditional HDS catalysts, such as $CoMo/\tau\text{-}Al_2O_3$ and $NiMo/\tau\text{-}Al_2O_3$. Over these catalysts, the first step is the partial or total hydrogenation of the heterocyclic ring -- at equilibrium at normal operating conditions -- and the rate-limiting step is the scission of the C-N-C bonds. Therefore an increase in the rate of C-N-C scission produces an overall increase in the HDN yield.

In this project it is proposed that the selectivity of the HDN reaction can be affected by an alteration of the catalyst acidity since it is possible that an acidic Hofmann-like deamination pathway is operative [1] in parallel with the hydrogenolysis of saturated C--N--C bonds. Such was the conclusion from the study done of the denitrogenation of piperidine [3], where it was demonstrated that Bronsted acid sites are active for the denitrogenation of N-heterocycles, whereas Lewis sites are not.

To understand better the role of acidic sites when other sites are present, molybdena was supported on the series of acidic aluminas, and the resulting new acidity and molybdic phases were characterized [4]. The oxidized catalysts supported on silica-aluminas showed increases from 3 to 150% of weak, medium and strong acid sites, which were contributed for by the molybdena phases. The nature of those phases was affected by support composition. The silica-rich supports favor more reducible phases, which presumably will have different hydrogenation activities.

During this fourth quarter, the characterization of the supported molybdena was continued. It was necessary to ascertain what type of acidity (Bronsted or Lewis) was generated in the molybdena phases and how that acidity was affected by the loading and state of oxidation of Mo. This latter aspect is relevant in the utilization of the supported catalysts for HDN, where they actually work under reduced conditions.

EXPERIMENTAL

Synthesis of Supports

Silica-aluminas with a range of composition from 10-90 wt% silica were prepared. Separately, pure silica and gamma-alumina were also synthesized from the same precursors as the silica-aluminas. The supports were characterized by BET surface area, ammonia chemisorption and TPD, and IR of adsorbed pyridine. Details of the preparation and characterization results were given before [2].

Synthesis of Supported Mo Oxide Catalysts

Supported molybdena catalysts were prepared by the incipient impregnation method using ammonium heptamolybdate as a precursor. A series of 28 catalysts were prepared, containing 7 different support compositions and 4 different molybdena loadings [4].

The impregnated samples were equilibrated at room temperature and then dried at 110°C for 4 hours, and calcined at 550°C for 12 hours. The preparations were characterized by BET surface area, ammonia chemisorption and TPD, and temperature-programmed reduction, as detailed previously [4].

Reduction of Mo Oxide Catalysts before IR Spectroscopy

The catalysts were reduced in a flow reactor consisting of a 1/2"OD quartz tube heated by a tube furnace. Before reduction, the calcined samples were exposed to flowing He at 400°C for 1 h to remove moisture. Then 100 ml/min of H_2 was flown over the catalyst for 4 h at 500°C. The samples were cooled, exposed to air for less than 5 min, and transferred to the IR cell, which was equipped with an environmental chamber. There a subsequent reduction with H_2 for 1 h at 500°C was produced. This two-part procedure ensured a deep bulk reduction in the first step, and a re-reduction of the surface Mo in the second step. It must be noticed that a one-step complete reduction in the IR cell was not possible, because of the high partial pressure of moisture that resulted from the low H_2 flowrate attainable through the cell and sample.

Ammonia Chemisorption

Pulses of NH_3 in 100 ml/min of He carrier were sent over the samples contained in a quartz 1/2"OD tube. The measured NH_3 pulses were detected with a thermal conductivity detector, after dosing at 120°C every 15 min until saturation was observed. The temperature of 120°C was chosen to completely avoid the physisorption of NH_3 on the catalyst. Before chemisorption, the catalyst was pretreated at 500°C under He flow.

Infrared Spectroscopy of Chemisorbed Pyridine

A Perkin-Elmer 1720 FTIR and computer were used to collect and process infrared spectra of adsorbed pyridine. This spectrometer was equipped with a Spectra Tech diffuse reflectance IR cell that included an environmental chamber. The catalysts in the oxidic state were pretreated in-situ at 450°C under He flow for 1 h and cooled to 200°C, and the catalysts in the reduced state were cooled to 200°C in H_2, before taking a blank spectrum. Pyridine was then adsorbed up to saturation at 200°C, by injecting 2 μl pulses of dried pyridine in a reservoir located upstream the cell and maintained at room temperature. Under those conditions, all of the pyridine was carried over the sample within 20 min. In order to prevent strong adsorption of pyridine in the tubings and prolonged bleeding from them, all tubes and valves had to be neutralized with KOH. After purging pyridine vapor with He, the IR spectra of adsorbed pyridine were recorded at 200°C. The spectral information was manipulated with Micro-Search, software supplied by Sprouse Scientific Systems.

The spectra presented below correspond only to the region of 1400 to 1700 cm^{-1}, which contains bands that pertain to pyridine adsorbed on Lewis and Bronsted acid sites. The band at 1447 cm^{-1} is characteristic of Lewis sites (LPy) while the band at 1548 cm^{-1} indicates Bronsted sites (BPy); the band at 1492 cm^{-1} is a combination one [5]. The areas under the bands are proportional to the abundance of their respective type of site. Since the extinction coefficients were not measured, the absolute amount of acid sites can not be calculated. Furthermore, the ratio of extinction coefficients $\epsilon^{L}_{1450}/\epsilon^{B}_{1545}$ is a function of solid composition and measurement and pretreatment conditions [6]. Therefore, the relative ratios of areas BPy/(BPy+LPy) presented below indicate only a trend in the abundance of Bronsted acid sites.

RESULTS AND DISCUSSION

Table 1 presents the total acidity of original supports and of oxidized and reduced catalysts. Only the 8 wt% MoO_3 is given, as an illustration of the general behavior of all molybdena catalysts. The last two columns of the table give the increase in the amount of acid sites with respect to the acidity of the support, when molybdena is present in oxidic or reduced forms. The same information can be seen in Fig. 1.

The maximum total acidity occurs in the region of 10-25 wt% silica, although the maximum gain in acidity produced by molybdena occurs at 75-90 wt% silica. Substantial acidity is lost during reduction of supported molybdena, but the reduced catalysts are still more acidic than the original supports. A comparison of this information with that derived from TPR [4] suggests that the new acid sites generated by the addition of molybdena are located on the reducible clustered molybdena phases (which we named β phases), and not on the highly dispersed phases (α phases) or on the support. Thus, alumina-supported molybdena, which is mostly in α phases, produces small gain in net acidity; on the other hand, silica-alumina-supported molybdena, which is largely in β phases, produces large gains in acidity. Silica, which contains only β phases, has the greatest %increase of acidity, but as shown before [4], contains exclusively weak acidity. A clearer description of the type and nature of the new acid sites created will be given after examining the IR results.

Table 1

Total Acidity of Supports and Catalysts
[mmol NH_3/g]

wt% Silica	Support	8 wt% MoO_3		increase, mmol NH_3/g	
		oxidic	reduced	oxidic	reduced
0 (Al_2O_3)	.304	.313	.321	.009	.017
10	.503	.517	.531	.014	.028
25	.512	.583	.547	.071	.035
50	.438	.530	.499	.092	.061
75	.269	.470	.358	.201	.089
90	.162	.404	.257	.242	.095
100 (SiO_2)	.001	.197	.100	.196	.099

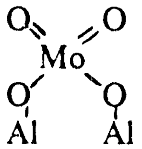
Fig. 2 shows the 1400-1700 cm^{-1} IR region for adsorbed pyridine on 8 wt% MoO_3/silica-aluminas. Other MoO_3 loadings produced similar spectra. The distinctive features on oxidic as well as reduced catalysts are: (a) silica-supported molybdena generates only Lewis acid sites, (b) silica-alumina-supported molybdena contains both Lewis and Bronsted acids, and (c) alumina-supported molybdena also contains both types of sites, although alumina support per se does not contain Bronsted acid sites.

Evaluating the areas under the 1447 and 1548 cm^{-1} bands, and assuming a ratio of extinction coefficients $\epsilon^{L}_{1450}/\epsilon^{B}_{1545} = 1$ for all catalysts, we can plot the relative abundance of Bronsted acid sites as a function of support composition, as in Fig. 3 for oxidic molybdena and Fig. 4 for reduced molybdena catalysts. In general, the oxidic as well as the reduced catalysts contain maximum amount of Bronsted acid sites in the range 75-90 wt% SiO_2, which does not coincide with the range for maximum amount of total acidity (Fig. 1). Upon reduction of molybdena, the Bronsted acidity drops uniformly for all support compositions, but in much larger proportion than the drop in total acidity (Table 1).

A closer look at Figs. 3 and 4 indicates that the B/L ratios for catalysts with low molybdena loading (≤ 4 wt%) are larger than those for the supports and follow the overall shape of the support curve. On the other hand, as the molybdena loading is increased, the B/L curves lose correlation with the support curve, and for a reduced 12 wt% MoO_3 catalyst the B/L ratio is almost independent of the support, except for pure silica support.

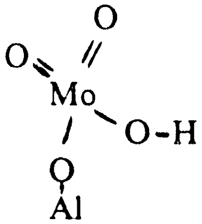
These results can be interpreted in terms of a simple model that takes into account the density of reactive OH groups on the support. The maximum density occurs on alumina, and the minimum one on silica. As the alumina is diluted with silica, the OH density falls and the number of surface Si-O-Al groups increases. The Si-O-Al groups are responsible for the support Bronsted acidity, being maximum at 75-90 wt% silica. During impregnation of ammonium heptamolybdate at close to neutral pH, monomeric and polymeric oxo-Mo species react with the support OH groups to form dispersed Mo phases. When the available OH groups have been saturated, the remaining oxo-Mo species precipitate on all of the surface during drying and agglomerate during calcination to minimize the surface free energy.

For low molybdena loadings (esp. 2 wt%), mostly dispersed oxo-Mo species (I) are being formed on alumina and possibly some silica-aluminas (≤ 25 wt% silica). These species do not affect the support Bronsted or Lewis sites, or at most consume as many Lewis sites as they recreate. Such species



(I)

demand a continuous alumina surface. The doubly-anchored di-oxo species might be expected to induce stronger acidity on nearby acid sites on the support, but we can not produce any conclusive evidence of this happening. At ≥25 wt% silica, the OH density is less and the alumina surface is more discontinuous, thus even though dispersed Mo phases are formed for 2 wt% loading, a predominance of mono-dentate di-oxo species (II) is likely:



(II)

This species is Bronsted acidic, and is responsible for generating new Bronsted acid sites. The maximum increase in total acidity and ratio of Bronsted sites occurs between 75 and 90 wt% silica, which is also the region where the maximum number of surface Si-O-Al groups appear, causing the maximum discontinuity of alumina and maximum appearance of mono-dentate Mo species II. The previous discussion is valid for very low contents of Mo (about 2 wt%). As the Mo content increases the abundance of II also increases as does the appearance of polymolybdates. The accompanying Bronsted site increment that is observed in Fig. 3 for silica:aluminas ≤50 wt%, is a consequence of the abundance of species II that is favored by the high density of OH. For silica:aluminas >50 wt%, the density of OH is so low that polymolybdates are formed, by condensation of species II, or by direct precipitation of polymolybdates from the impregnating solutions. Therefore Fig. 3 shows that the optimum loading for maximum occurrence of species II and Bronsted sites is 4 wt% MoO_3. Reduction with H_2 decreases the number of Bronsted acid sites, possibly by reducing the di-oxo structure II. It must be noticed that this model of generated acidity can also explain Segawa and Hall's results of surface acidity on molybdena/alumina catalysts [7].

In the model proposed here, the new Lewis acid sites are formed mainly on polymolybdates species, due to coordinative unsaturation of Mo. Such unsaturation, and consequently Lewis sites, should increase in amount as Mo is reduced, a fact which is verified by Fig. 4. The result is most noticeable for 12 wt% Mo loading, which contains a major fraction of polymolybdate species, and displays the largest decrease in B/L ratio upon reduction. Silica support is unable of generating species II, thus its B/L ratio is zero for all MoO_3 loading. MoO_3 on silica is present exclusively as low-dispersed polymolybdate species, and these species are responsible for the Lewis acidity present.

CONCLUSIONS

The formation of new acidity upon deposition of molybdena on silica-alumina supports has been explained on the basis of total acidity measurements, TPR, and infrared spectroscopy of adsorbed pyridine. The new acidity is of both Lewis and Bronsted type, the preponderance of one over the other depending on support composition, as well as loading and state of oxidation of Mo. High-alumina supports and low Mo loading favor dispersed Mo species. It was postulated that a monodentate Mo species is responsible for the new Bronsted acidity, while a bidentate di-oxo species does not generate new acidity. Coordinative unsaturation of polymolybdates is responsible for the new Lewis acidity, which is increased upon reduction of Mo. High-silica supports favor monodentate species (high Bronsted acidity) up to 4 wt% MoO_3. Beyond that, polymolybdate species and Lewis acidity predominate. Reduction with H_2 causes the appearance of more coordinative unsaturation (more Lewis sites) and the reduction of the monodentate Mo species (less Bronsted sites).

ACKNOWLEDGEMENTS

Funding

This work was carried out with funds from DOE (Grant DE-FG22-89PC89771), partial support from NSF (Grant No. RII-8610671) and from the Commonwealth of Kentucky (EPSCoR Program).

Personnel

Jorge Marzari, Master of Science student
S. Rajagopal, Post-Doctoral Research Associate

REFERENCES

1. N. Nelson and R. B. Levy, J. Catal. 58(1979)485

2. R. Miranda, "Mechanism of Hydrodenitrogenation. Part I: Preparation and Characterization of Acidic Supports", DOE Report DOE/PC/89771-1, January 1990.

3. R. Miranda, "Mechanism of Hydrodenitrogenation. Part II: Piperidine Denitrogenation over Silica-Aluminas", DOE Report DOE/PC/89771-2, April 1990.

4. R. Miranda, "Mechanism of Hydrodenitrogenation. Part III: Preparation and Characterization of Acidic Molybdena Catalysts", DOE Report DOE/PC/89771-3, July 1990.

5. K. Tanabe, in Catalysis: Science and Technology (J.R. Anderson and M. Boudart, Edt.) Springer-Verlag, Berlin, 1981, v.2, p.231; M.C. Kung and H.H. Kung, Catal. Rev.-Sci. Eng. 27(1985)425

6. J.W. Ward, J. Catal. 11 (1968)271; M.R. Basila, T.R. Katner and K.H. Rhee, J. Phys. Chem. 68(1964)3197

7. K. Segawa, W.K. Hall, J. Catal. 76(1982)133-143

FIGURES

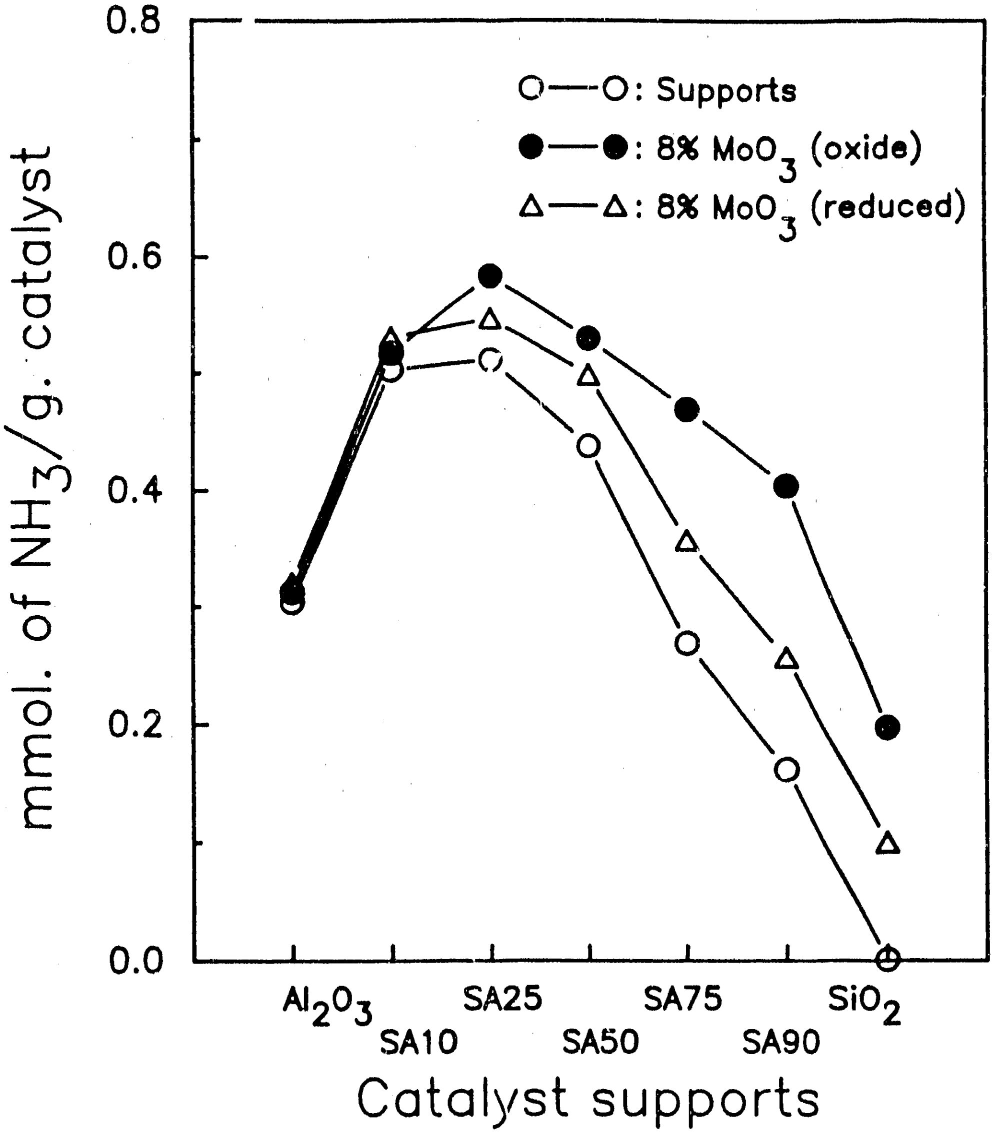


Fig. 1 Total acidity of oxidic and reduced molybdena catalysts over acidic supports.

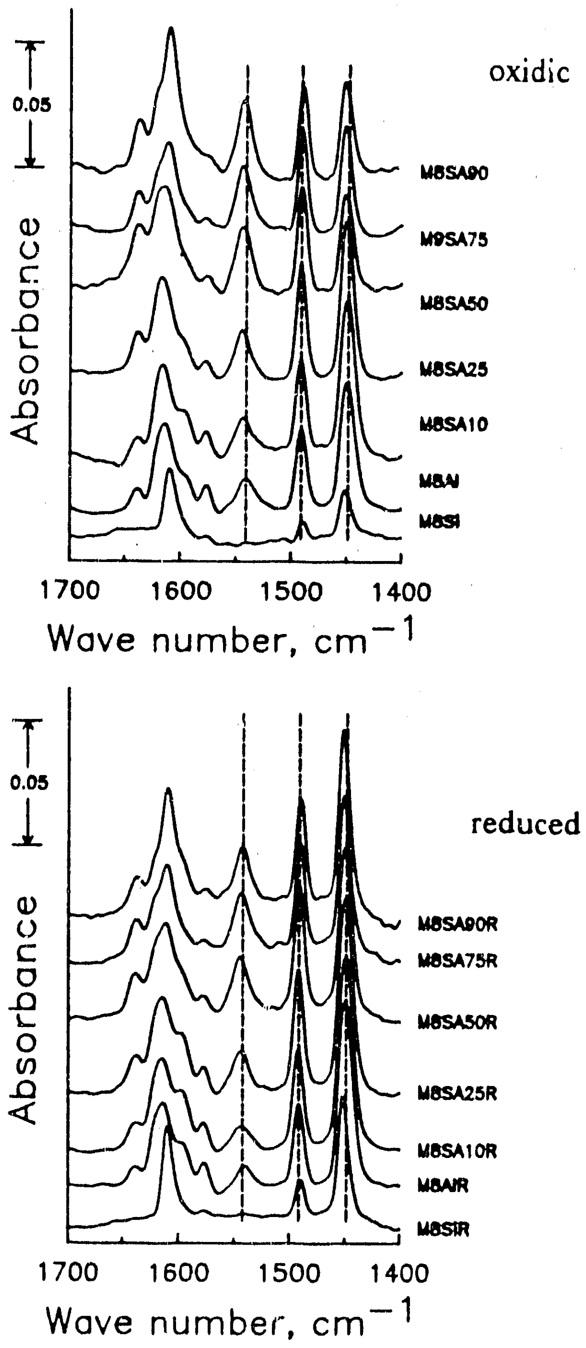


Fig. 2 IR spectra of chemisorbed pyridine on oxidic and reduced molybdena catalysts on supports of varying acidity.

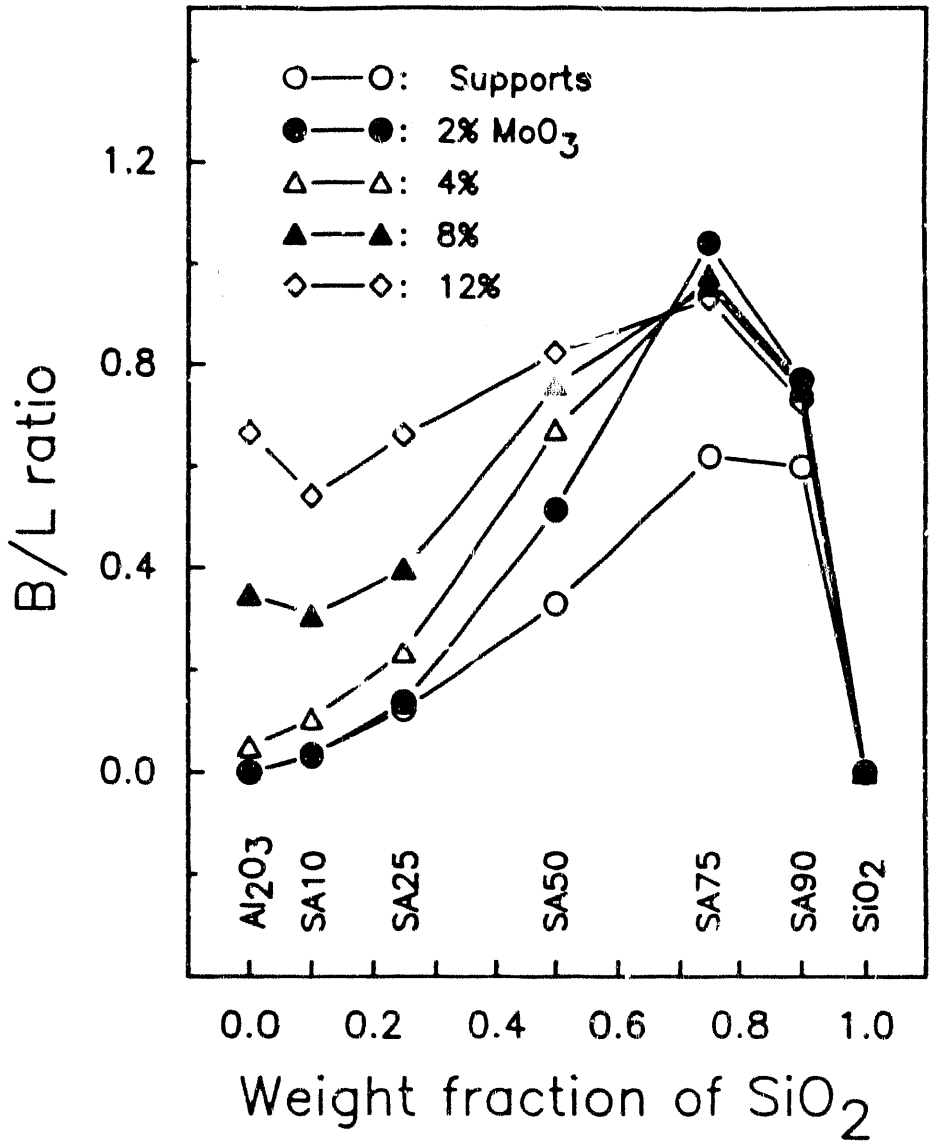


Fig. 3 Ratio of Bronsted to Lewis acidity for oxidic molybdena catalysts.

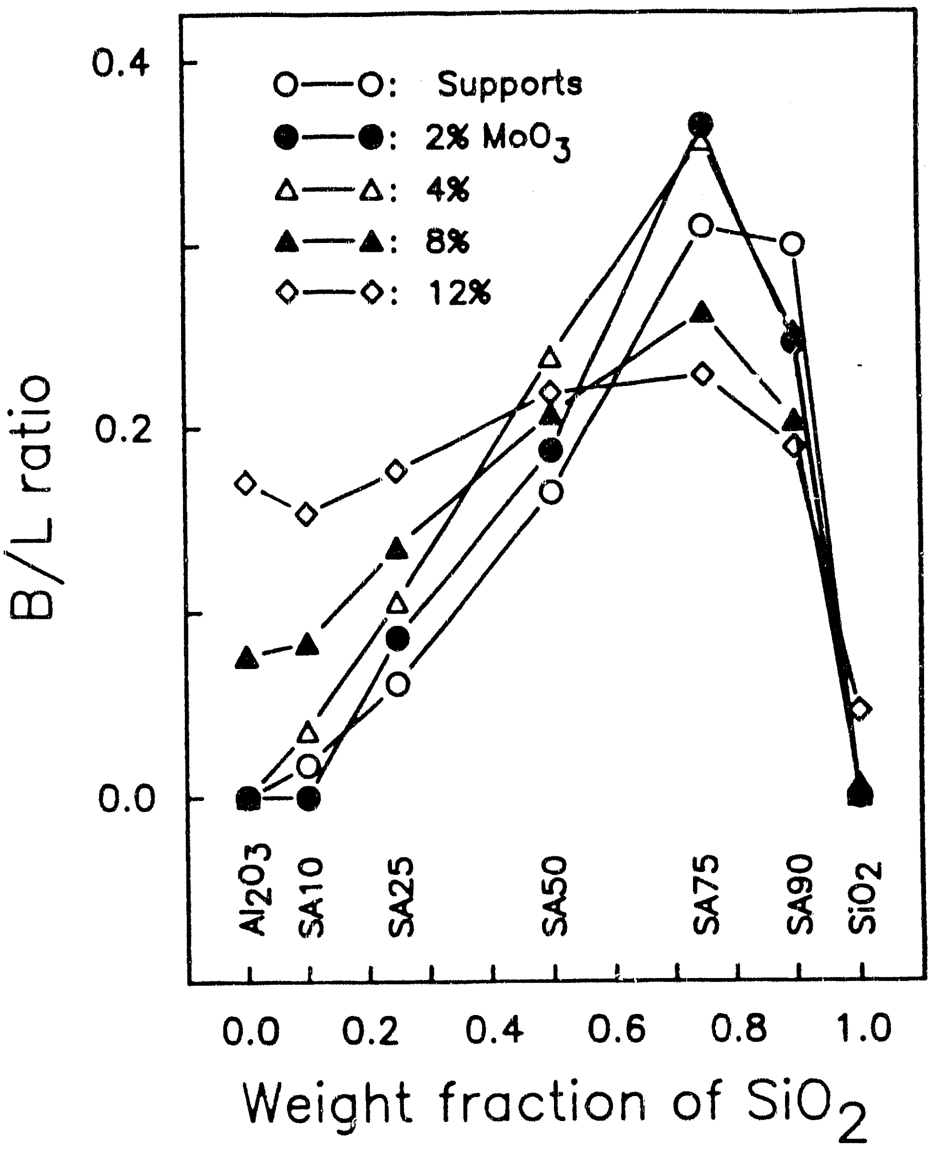


Fig. 4 Ratio of Bronsted to Lewis acidity for reduced molybdena catalysts.

END

DATE FILMED

12 / 12 / 90